

Degradation of methyl green by a supported photocatalyst: Economic technique for the depollution

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Abstract

The photocatalytic degradation of (4-{[4-(dimethylamino) phenyl] [4-(trimethylazaniumyl) phenyl] methylidene} cyclohexa-2,5-dien-1-ylidene) (dimethyl) ammonium bromide chloride called methyl green (MG) is taken as a model to study the reduction of wastewater treatment costs using thin film photocatalysis. The photocatalyst used is zinc oxide supported on glass, by a simple and economical method of pyrolysis spraying, enabling to decrease the cost of photocatalyst recovery after water treatment. The concentration of aqueous solution of VM was 10^{-4} M. Doping of zinc oxide with aluminum (5%) significantly improved the photocatalytic degradation of MG. Under visible irradiation, the apparent rate of degradation was 10^{-2} min^{-1} and $3.3 \times 10^{-2} \text{ min}^{-1}$ for ZnO and ZnO:Al (5 %), respectively. When the free solar radiation is used, the result of the photocatalysis is very satisfactory with an apparent constant of $2.7 \times 10^{-2} \text{ min}^{-1}$ for the doped photocatalyst ZnO:Al (5 %).

Keywords: Methyl Green, Photocatalysis, Supported Zinc Oxide, Water Treatment, Solar Irradiation

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1. Introduction

Global demand for organic dyes and pigments continues to grow as they are used in various fields such as textiles, printing, painting, and other industries; and this flourishing market will still develop in the future. However, more than 11 % of the world's annual dye production (approximately 0.7 million tons) is rejected annually by the various industries in the form of industrial effluents [1], and the contamination of natural waters by dyes has become one of the main forms of pollution, and hence, all the countries of the world are concerned with the development of new treatment methods [2, 3]. The discharge of these wastewaters loaded with dyes will lead to serious environmental problems and impacts on human health, because of their toxicity, and causes considerable damage to the aquatic environment because they are mortal for marine organisms (fish, algae, bacteria, etc.) moreover, they are mutagenic, carcinogenic, genotoxic to humans. Some dyes may cause allergic and dermatological reactions, with a possibility of bioaccumulation in living organisms and therefore their persistence in the food chain. Heterogeneous photocatalysis are among the most effective techniques for Azizi et al., 2020

the treatment of dyes in polluted waters. This technique is based on the excitation of a semiconductor by light energy for the degradation of pollutants organic molecules into water (H₂O) and carbon dioxide (CO₂) molecules and other mineral compounds [4-13]. The mechanism of photocatalysis is largely explained in bibliography [14-18]. As a photocatalyst, we chose to use zinc oxide (ZnO) due to its photocatalytic activity better than that of the famous TiO₂ [19-21]. We carried out three (03) improvement operations namely: the semiconductor, the material used and the light source in order to finally suggest an efficient and economical photodegradation technique.

The first operation: The deposition of zinc oxide (ZnO) on glass supports, by a simple and economical method of pyrolysis spray. It allows the elimination of the cost recovery of the photocatalyst suspensions after photocatalytic treatments.

The second operation: The widening of the absorption domain of Zinc Oxide (ZnO) towards larger wavelengths by doping with aluminum (Al).

The third operation: The replacement of expensive artificial light energy by free and renewable solar energy.

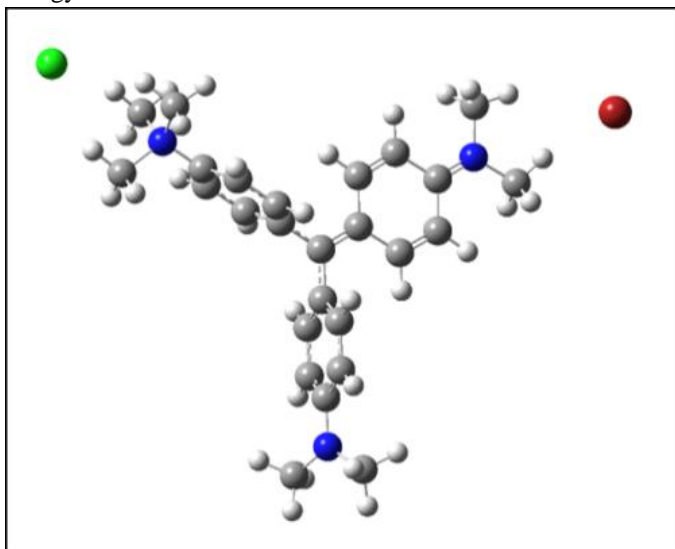


Figure 1: Molecular structure of Methyl Green (MG)

2. Materials and methods

All the chemicals used in this work are of analytical quality and used without any prior purification; and all the solutions were prepared with bi-distilled water.

2.1. Deposition of the photocatalyst (ZnO) on a support

The metals oxides were deposited on glass substrates by the Spray Pyrolysis technique described in the literature [22] by scattering the Zinc solution at a deposition temperature of 400 °C; the distance between the beak and the substrate was fixed to 3 cm, with a deposition time of 20 min and a flow rate of 1 mL/min. The concentration of dihydrated zinc acetate solution ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) was 0.1 mol/L. The optical T (λ) transmission spectra of the supports were obtained using the JASCO V630 DUO/5G UV-VISNIR dual beam spectrophotometer. The photodegradation of MG by ZnO can be done using solar irradiation as reported by Mai et al [23]. In order to repeat the same test with our supported photocatalyst, the ZnO was doped with aluminum to widen its absorption range towards the visible radiation, since the ZnO photocatalyst requires excitation with a wavelength less than 400 nm. The amount of light collected in the UV region is only about 5 % of the solar spectrum [24, 25].

2.2. Doping photocatalyst ZnO with aluminum (5 %)

The doping of ZnO with aluminum (Al) 5 % is realized by the preparation of a solution of a zinc acetate and aluminum sulfate 0.095 M and 0.005 M respectively. This doping permits the shift of the UV-visible absorption spectrum of the ZnO towards longer wavelengths allowing the use of the direct solar irradiations.

2.3. The reactor and the light sources

The photochemical reactor is a rectangular shaped glass of dimension: 55.5 cm long, 11 cm wide and 7 cm in height and consists of three parts: the first part is the starting tank of the solution, the 2nd compartment is a tray on which the support of photocatalyst is deposited with an inclusion angle of 2°; and the third part is the return tank of treated solution. The reactor is equipped with a variable flow pump connected to the two tanks with piping. A light source is placed 7 cm above the reactor of irradiation. Two types of lamps were used as a light source:

The first: A fluorescent tube of type "Philips TLAD 15W/05" with an emission spectrum having a maximum at around 365 nm with a half-band width of 50 nm (Figure2).

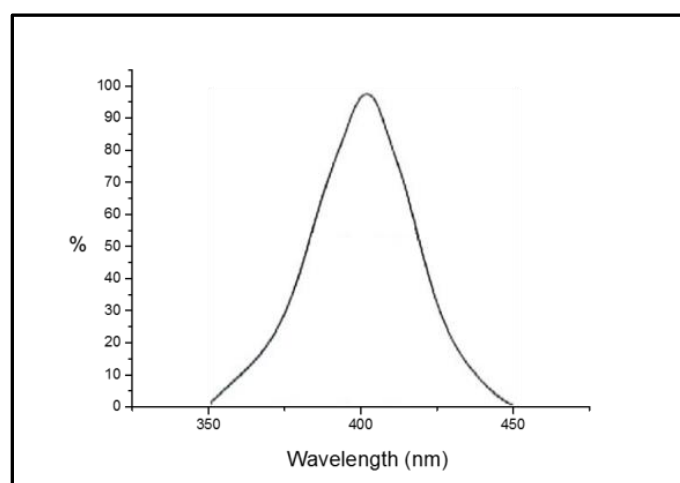


Figure 2: Emission spectrum of the polychromatic lamp Philips TLAD 15W/05

The second: A lamp of the type OSRAM ULTRA-VITALUX 300W, which emits essentially in the visible (Figure3.). These lamps are heated 25 to 30 minutes before the start of photocatalysis tests under illumination.

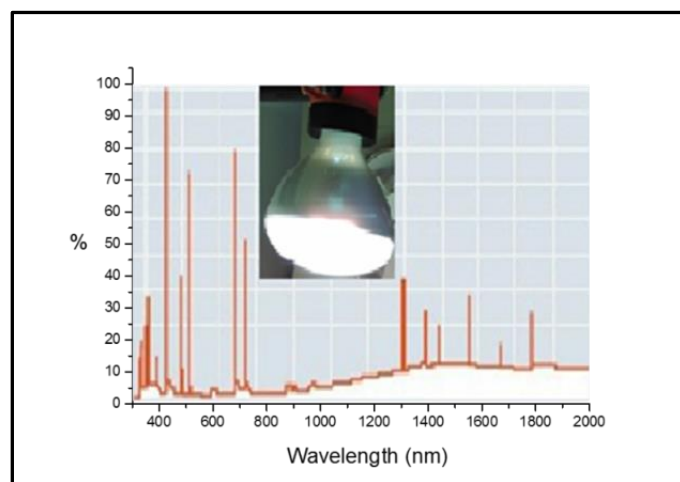


Figure 3: Spectrum of the lamp ULTRA-VITALUX 300W OSRAM

2.4. MG photodegradation in aqueous solution

A volume of 150 ml of MG aqueous solution (10^{-4} M) was irradiated in the reactor already mentioned. The kinetics of the photocatalytic degradation were followed by UV-visible spectroscopy at the maximum wavelength of the GM absorption (at $\lambda_{max}=632\text{nm}$). The UV-visible absorption spectrum of the MG is illustrated in (Figure4.).

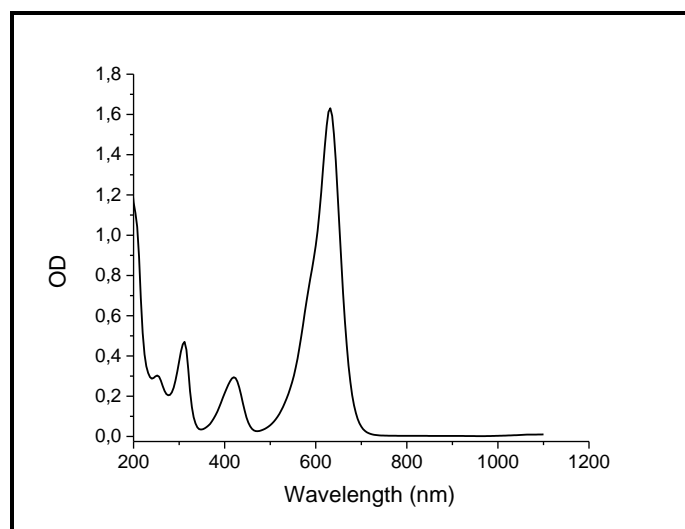


Figure 4: UV-visible spectrum of aqueous solution [MG]= 10^{-4} M

2.5. Photocatalytic degradation study by solar irradiation

After the satisfactory results of MG photodegradation, we process to MG photocatalysis by ZnO: Al (5%) photocatalyst under free and renewable solar irradiation, using the same photochemical reactor. Photodegradation by sun irradiation was realized during the day 05/04/2018, between 10h and 14h, at Larbi ben M'Hidi University of Oum el Buaghi, GPS coordinates ($35^{\circ}52'48.99''\text{N}$) and ($7^{\circ}5'27.62''\text{E}$).

3. Results and discussions

3.1. Comparison of direct photodegradation of MG by lamps

Comparison of MG photocatalytic degradation kinetics by the two lamps is displayed in Figure5. The best degradation rates are attributed to photocatalysis under irradiation between 350 and 450 nm with 15% and 5% for essentially visible radiation, for 90 minutes of irradiation. The rate of photocatalytic degradation during the emission between 350 and 450 nm is three (03) times better than irradiation in visible because the emission spectra of first lamp is more energetic than the second.

3.2. MG photocatalytic degradation kinetics study in aqueous solution

Adsorption is the preliminary step of photocatalysis [26]. To determine its adsorption value in the dark, we placed a solution of MG (10^{-4} M) in the photochemical

reactor under the same conditions as photocatalytic degradation and in the dark.

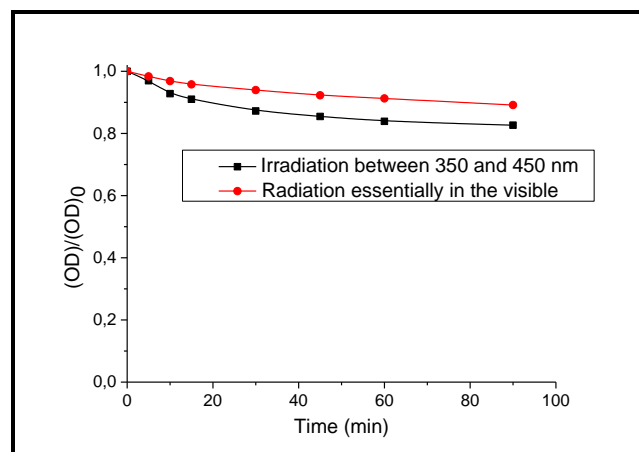


Figure 5: Comparison of the kinetics of direct photodegradation of MG (10^{-4} M), irradiated by wavelengths between 350 and 450 nm and essentially in visible

We found that the adsorption/desorption equilibrium is reached after 10 minutes with an adsorption rate of 15%. The photocatalytic studies were carried out on MG aqueous solution (10^{-4} M) with three different sources of light: the two lamps already mentioned and the solar light, in the same photochemical reactor. The entire surface of the photochemical reactor plate is covered with photocatalyst thin layer. We used two photocatalysts, namely ZnO and ZnO/Al (5%).

3.2.1. Irradiation between 350 and 450 nm

MG photocatalytic degradation kinetics, with ZnO and ZnO/Al (5%) thin layers were realized at 632nm (Figure6). Photocatalytic degradation kinetics is of first order [27, 29] and the best degradation rates are obtained by the ZnO/Al (5%) thin layer, with 52% degradation after 90 minutes and 34% for the ZnO thin layer for the same irradiation time. The apparent rate constants are derived from the plot of $\ln[(OD)_0/(OD)]$ as a function of time (Figure7) and are equal to $15.2 \times 10^{-2} \text{ min}^{-1}$ and $29.9 \times 10^{-2} \text{ min}^{-1}$ for thin layers of ZnO and ZnO/Al (5%), respectively. Aluminum doping (5%) improves MG photocatalytic degradation by double increasing the degradation apparent rate constant. This result can be explained by the shift of the UV-visible absorption spectrum of ZnO after doping to longer wavelengths [30-32].

3.2.3. Irradiation essentially in the visible

MG solution irradiated essentially in the visible with ZnO and ZnO/Al (5%) thin layers shows different photocatalytic degradation kinetics (Figure 8). The degradation rates were respectively 40% and 58% after 90 minutes of irradiation.

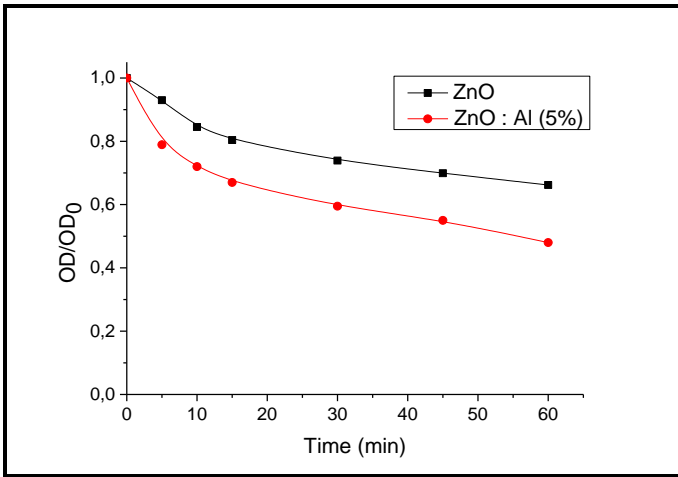


Figure 6: comparison of MG (10^{-4} M) photocatalysis kinetics, irradiated at wavelengths between 350 and 450 nm, with the presence of metals oxides thins layers

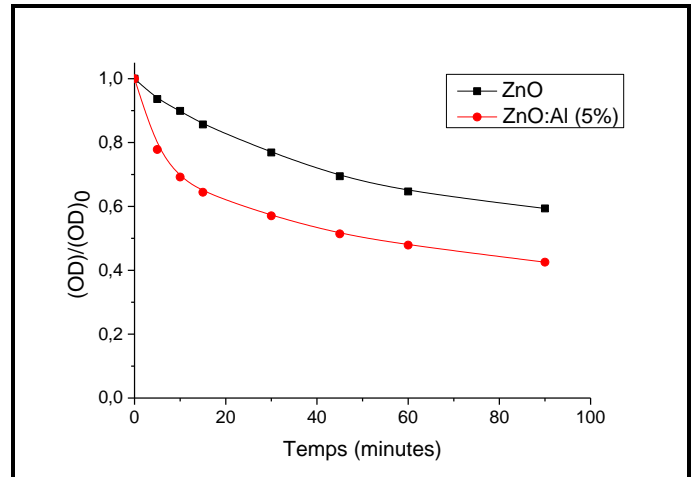


Figure 8: Comparison of MG (10^{-4} M) photocatalysis kinetics, irradiated at visible wavelengths, with ZnO and ZnO/Al (5%) thins layers

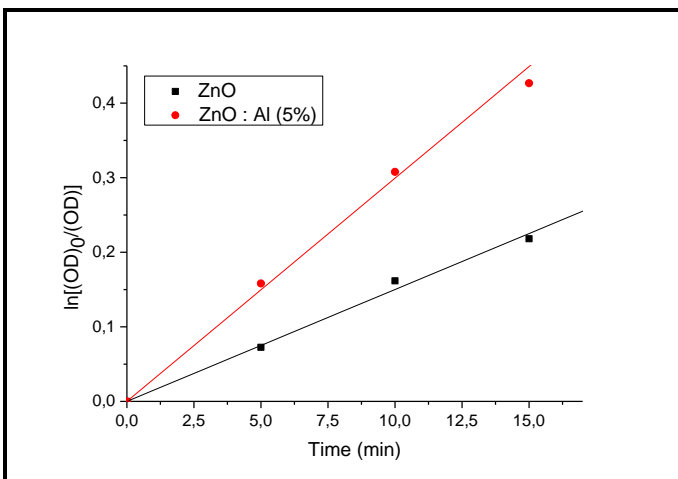


Figure 7: $\ln [(OD)_0/(OD)]$ variation as a function of time, during MG (10^{-4} M) solution photocatalysis, irradiated at wavelengths between 350 and 450 nm, with presence of metals oxides thins layers

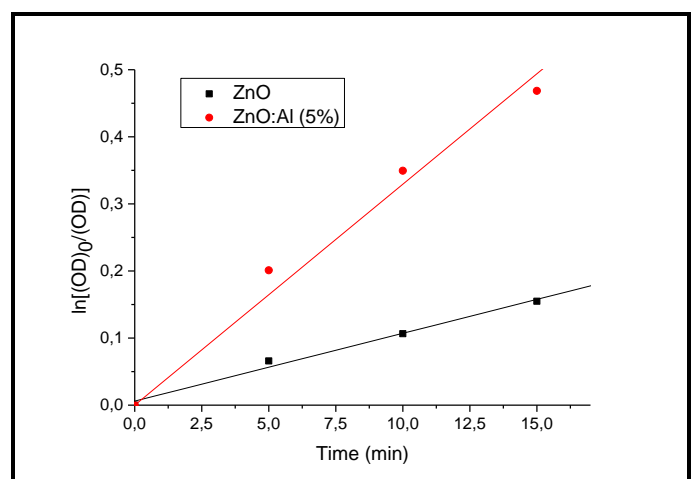


Figure 9: $\ln [(OD)_0/(OD)]$ variation as a function of time, during MG (10^{-4} M) solution photocatalytic degradation, by metal oxides thins layers, irradiated essentially in the visible

3.2.4. Solar irradiation

MG solution UV-visible spectrum evolution (Figure 10) during the photocatalytic degradation shows a decrease of absorbance of the main band and a change in the absorbance of the other bands, indicating MG photodegradation and photoproducts apparition. MG photodegradation kinetics by ZnO/Al (5%) thin films under solar irradiation illustrated in the figure 11 shows a degradation rate of 52% for an irradiation time of 90 minutes. The apparent rate constants is $2.7 \times 10^{-2} \text{ min}^{-1}$, and it's derived from the plot of $\ln [(OD)_0/(OD)]$ as a function of time (Figure 12). This result is very promising to replace the lamps with solar light which is free and renewable. Apparent rate constants are 10^{-2} min^{-1} and $3.3 \times 10^{-2} \text{ min}^{-1}$ for thin layers ZnO, and ZnO/Al (5%), respectively (Figure 9).

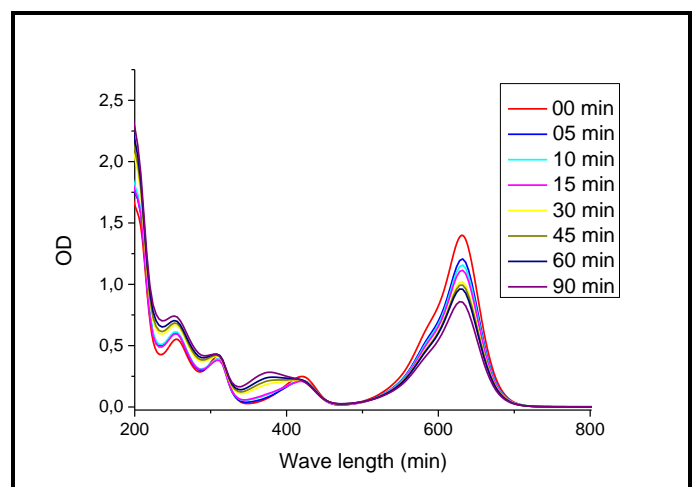


Figure 10: MG (10^{-4} M) solution UV-Visible spectrum evolution, through photocatalytic degradation with thin layer of ZnO:Al (5%) presence, under solar irradiation

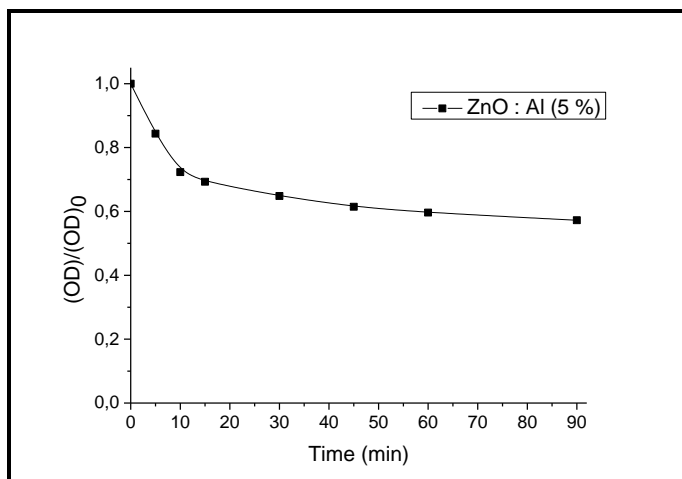


Figure 11: MG (10^{-4} M) photocatalytic kinetics, under solar irradiation by ZnO/Al (5%) thin layer

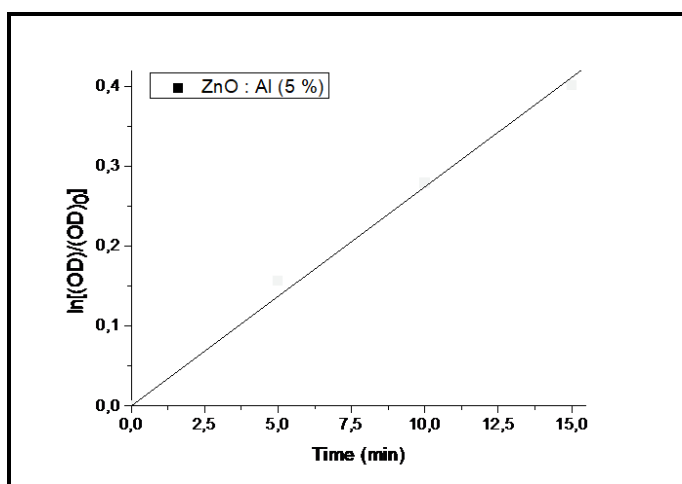


Figure 12: $\ln [(OD)/(OD)_0]$ variation as a function of time, during MG ($[MG]=10^{-4}$ M) photocatalytic degradation, under solar irradiation by thin layer of ZnO:Al (5%)

4. Conclusions

This work dealt with the MG degradation by photocatalysts thin layers supported on glasses using the Spray Pyrolysis method which was averred as a suitable method for the replacement of the high cost recovery technique of the semiconductors in suspension after photocatalytic treatment.

MG photocatalytic degradation was studied as well under different conditions of light sources using the photocatalyst (ZnO). Moreover, the doping of the ZnO by aluminum (Al:5%) has considerably improved MG photocatalysis.

The best results were obtained by the lamp which emitting essentially in the visible which proves that the doping of the ZnO by aluminum (Al:5%) makes it possible to shift UV-visible absorption spectrum towards the longer wavelengths.

MG photocatalytic degradation under solar irradiation has given promising results and has shown that AZIZI *et al.*, 2020

we can replace artificial and expensive light sources by free and renewable solar energy.

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